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TITLE: METHOD FOR REVAMPING FIXED-BED CATALYTIC REFORMERS

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METHOD FOR REVAMPING FIXED-BED CATALYTIC REFORMERS

FIELD OF THE INVENTION

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[0001] The invention relates generally to catalytic reformers. More particularly, the invention relates to an improved method for converting or revamping high pressure, fixed-bed catalytic reformers to catalytic reformers with continuous, moving-bed reactors.

10 CROSS REFERENCE TO RELATED APPLICATION

[0002] This application claims priority from U.S. Provisional Application No. 60/421892, filed 29 October 2002.

BACKGROUND OF THE INVENTION

15 **[0003]** Catalytic reforming is an established refinery process. It is used for improving the octane quality of hydrocarbon feeds. Generally, reforming refers to the total effect of molecular changes, or hydrocarbon reactions on the hydrocarbon feed, produced by a number of reactions. Typical reforming reactions include dehydrogenation of cyclohexanes, dehydroisomerization of alkylcyclopentanes,
20 dehydrocyclization of paraffins and olefins, isomerization of substituted aromatics, and hydrocracking of paraffins. Typical reforming catalysts are multifunctional catalysts having a hydrogenation-dehydrogenation component dispersed on a porous, inorganic oxide support. The support may typically also contain an acid functionality needed for the reforming reactions.

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[0004] Reforming reactions are both endothermic and exothermic. Endothermic reactions are typically predominant in the early stages of reforming. Exothermic reactions are predominant in the later reaction stages. A reforming unit typically comprises a plurality of serially connected reactors with furnaces for supplying
30 additional heat to the reaction stream as it passes from one reactor to the next in order to compensate for the heat taken up in the overall endothermic character of the process. Conventionally, reforming processes have been operated as semiregenerative or cyclic processes using fixed bed reactors or continuous processes using moving bed reactors. Proposals have also been made for combining fixed and
35 moving bed reactors with the regeneration mode being appropriate to the reactor types

used in the hybrid configuration, so that the fixed bed reactors have retained the fixed bed type regeneration, usually semiregenerative, and the moving bed reactors in the unit have retained the dedicated moving bed regenerator. Units of this hybrid type are disclosed, for example, in US 5,190,638; US 5,190,639; US 5,519,611; US 5,521,838; US 5,522,463; US 5,354,451; US 5,368,720 and US 5,417,843. The unit described in US 5,417,843 uses two trains of fixed bed reactors with each train having a final moving bed reactor at the end and the moving bed reactors sharing a moving bed regenerator. The unit shown in US 5,190,639 uses two trains of fixed bed units feeding into a shared moving bed reactor with its own dedicated, fully integrated regenerator. Similar hybrid reforming units using combinations of fixed bed and moving bed reactors are described in NPRA Paper No. AM-96-50 "IFP Solutions for Revamping Catalytic Reforming Units" (1996 NPRA Annual Meeting, 17-19 March 1996). US 4,498,973 describes a moving bed reforming unit in which two moving bed reactor stacks share a common regenerator. UOP has recently announced its CycleX™ Process for increased hydrogen production from a fixed bed reforming unit by the addition of a circulating catalyst reactor as the final reactor in the reactor sequence. This reactor is provided with its own heater and regenerator as an expansion of existing assets rather than as a substitution of them: NPRA Paper AM-03-93.

[0005] In semiregenerative reforming, the entire reforming process unit is operated by gradually and progressively increasing the temperature to compensate for deactivation of the catalyst caused by coke deposition, until finally the entire unit is shut-down for regeneration and reactivation of the catalyst which is carried out with the catalyst remaining in the reactor cases. In cyclic reforming, the reactors are individually isolated by various piping arrangements. The catalyst is regenerated and then reactivated while the other reactors of the series remain on line. A "swing reactor" temporarily replaces the reactor which is removed from the series for regeneration and reactivation of the catalyst, which is then put back in the series. In continuous reforming, the reactors are moving-bed reactors with continuous or intermittent addition and withdrawal of catalyst through which the catalyst moves progressively before it is passed to a regeneration zone for regeneration and rejuvenation before being returned once again to the reactor. In the regenerator, at least a portion of the deposited coke is burned off and the regenerated catalyst is

recycled to the reactor to continue the cycle. Commercial continuous reforming units may have the reactors arranged in a side-by-side or in a stacked configuration. Because the continuous mode of operation with its frequent regeneration can tolerate a higher degree of coke lay-down on the catalyst, it is possible to operate continuous units at lower pressures than those normally used with semi-regenerative and cyclic units in which it is important or at least desirable to extend catalyst life between successive regenerations.

[0006] Environmental concerns have driven the removal of lead from the gasoline pool and the introduction of premium grade, higher octane, lead-free gasoline in Europe and the United States. In response, petroleum refiners have changed the manner in which refinery units are run to meet the concomitant demand for higher octane, lead-free gasoline. Catalytic reforming units produce a major portion of the refinery gasoline pool and for this reason, improved reforming methods and units are needed for producing lead-free fuel products with adequate octane ratings. Reforming can also be an attractive source of hydrogen in the refinery, especially when the sulfur level of fuels must be reduced to meet government regulations.

[0007] Semiregenerative reforming units may be converted to continuous moving-bed units to take advantage of the improved yield of higher octane reformat and hydrogen associated with continuous operation but the conversions which have so far been considered are essentially entire unit replacements which require replacement of all existing vessels and most of the ancillary equipment as well as installation of an integrated catalyst regenerator which is one of the most costly items in the conversion. The cost of the regenerator can be as much as about 80 percent of the total cost required for the conversion. There is still a need, therefore, for an improved, less costly revamping method for converting fixed-bed reformer units to moving-bed reformer units.

SUMMARY OF THE INVENTION

[0008] The present invention relates generally to a technique for converting fixed-bed, catalytic reformer units to moving-bed catalytic reformer units. The costs of conversion associated with the present conversion technique will be significantly less

than existing conversions partly because the present technique makes use of existing facilities and does not require dedicated onsite continuous catalyst regeneration facilities. Another advantage of the present invention is that it allows a number of existing moving-bed catalytic reformers to share a single catalyst regeneration facility,
5 further reducing the investment required to convert several fixed-bed units.

[0009] According to the present invention, the technique for converting a fixed-bed catalytic reformer unit which has at least one fixed-bed catalytic reformer reactor to a moving bed unit converts the fixed-bed catalytic reformer reactor to a moving-bed
10 catalytic reformer reactor which allows continuous or intermittent addition of fresh or regenerated catalyst to its catalyst inlet and continuous or intermittent removal of spent catalyst from the catalyst outlet of the reactor. The unit is provided with catalyst feed facilities for continuously or intermittently charging fresh or regenerated catalyst in a continuous or intermittent mode of operation to the moving-bed reactor. In addition,
15 spent catalyst recovery facilities are added for collecting the spent catalyst, storing it temporarily, and transferring it to a catalyst regeneration facility. The moving-bed reactor, the catalyst feeding facilities and the catalyst recovery facilities are operatively connected between themselves and to the existing facilities (piping, ancillary equipment) of the fixed-bed unit that will not require replacement.

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[0010] The moving-bed reactor is operated at an effective pressure to improve reformate quality and yield compared to the quality and yield from the fixed-bed unit before the conversion. It is an advantage of the present invention that the moving-bed reformer reactors of the converted unit may be operated at an effective pressure that is
25 sufficiently low to improve substantially the reformate quality and yield as compared to the reformate quality and yield obtained from the fixed-bed unit before conversion. The pressure is, however, maintained during normal operation at a value which is sufficiently high to allow the use of some of the existing equipment of the fixed-bed catalytic reformer unit such as compression, heat exchangers and furnaces. The use
30 of a higher pressure than typical for a fully integrated continuous reactor-regenerator is desirable in that it enables the rate of catalyst flow for regeneration to be reduced (relative to that of an integrated unit) and so relieves the burden of catalyst handling.

[0011] An effective operating pressure for a converted reformer unit may typically be substantially lower than the operating reactor pressure of the fixed-bed unit. Typically, an effective operating pressure for the converted reformer unit may be from about 15 to about 70 percent, preferably from about 20 to about 60 percent, and
5 more preferably from about 25 to about 50 percent lower than the operating reactor pressure of the fixed-bed unit prior to conversion.

[0012] The present invention may employ an offsite catalyst regeneration facility. Alternatively, it may employ a community onsite continuous catalyst regeneration
10 facility, i.e., a continuous catalyst regenerator that is shared between more than one reactors. Also, a non-continuous onsite regeneration facility may be used for one or more catalytic reformer units.

[0013] Depending on site economics and other factors, it may be preferable to use
15 an offsite catalyst regeneration facility. Alternatively, a continuous regeneration facility may be located onsite near a plurality of converted reformers. Catalyst from the continuous reactors in the reformer units may be transported to the regeneration facility and, after regeneration, be transferred back to the reformers for re-use in the reactors. Transfer from the reactors to the regenerators may be continuous, e.g. by
20 suitable transfer devices, for example, by conveyers, or intermittently, for example, by truck or rail car, depending on the extent of site requirements, proximity of the regenerator and other factors. Another variation would be to use an onsite, non-continuous regeneration facility such as a cyclic type regenerator that can be used to regenerate catalyst from a plurality of moving-bed reformer units.

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THE DRAWING

[0014] Figure 1 shows a continuous moving-bed reforming process built from an existing high pressure fixed-bed reformer unit. Thicker lining indicates new equipment
30 and piping while thinner lining indicates existing equipment and piping.

DETAILED DESCRIPTION

5 [0015] The present invention provides a substantially lower cost option for refiners to make significant improvements to the performance and service factor of existing fixed-bed reformer units. Non-continuous (or fixed-bed) catalytic reformers could be semiregenerative catalytic reformers, swing-reactor (also referred to as cyclic regeneration reformers) catalytic reformers or hybrid systems, all of which are known.

10 [0016] The non-continuous catalytic reformer unit may be a semiregenerative unit. Semiregenerative units typically contain one or more fixed-bed reactors operating in series with inter-bed heaters to maintain operating severity as the catalyst deactivates by increasing the reaction temperature. Eventually, a semiregenerative unit is shut down for catalyst regeneration and reactivation.

15 [0017] Typically operating conditions for a semiregenerative reformer are:

pressure: 1035 to 3800 kPag (approx 150 to 550 psig)

temperature: 425 to 565°C (approx 800 to 1050°F)

space velocity: 0.5 to 3.0 WHW

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[0018] A high pressure semiregenerative catalytic reformer can be effectively converted to operate at a lower effective reactor pressure in the reactors of the converted unit to secure substantial improvements in reformate quality and yield (relative to the semiregenerative unit prior to conversion) but which does not create an insuperable problem of catalyst handling (charge, discharge, transfer, regeneration) once conversion has taken place. Specifically, the present invention method allows production of reformate preferably having an octane number of from 90 to 105, more preferably from 95 to 103, and most preferably from 98 to 102. In addition to the improved reformate quality and yield obtained, an effective reactor pressure, as used in the present invention, allows the use of existing facilities such as compression equipment, heat exchangers, furnaces, piping, drums and pumps.

35 [0019] This effective pressure is typically lower from the reactor pressure of typical semiregenerative units but also higher than with a typical continuous reactor where there are no similar constraints on catalyst rate created by handling considerations. It

may range from 345 to 2760 kPag (50 to 400 psig), preferably from 690 to 2620 kPag (100 to 380 psig), and more preferably from about 1035 to 2415 kPag (150 to about 350 psig).

5 **[0020]** The converted unit will be operated at an effective reactor pressure that provides substantially improved reformat quality and yield compared to existing fixed-bed reforming units. The extent of reduction in reactor pressure may be limited, if desired, to the extent that much of the existing compression, furnace, piping, etc., equipment can be reused with the new moving-bed reactors. Limiting the extent of the
10 pressure reduction also reduces the required catalyst circulation rate (between reactors and regeneration facilities). This is particularly attractive in a system where the spent catalyst is sent offsite for regeneration. Typically, a reactor pressure reduction of from about 25 to about 50% can be realized without having to replace most of the existing facilities. However, much larger pressure reductions may also be
15 used where it may be attractive under some site-specific conditions to replace much of the existing facilities.

[0021] Preferably, the fixed-bed reformer unit will be converted to a moving-bed reformer reactor that allows continuous addition of freshly regenerated catalyst to an
20 inlet of the reactor and continuous removal of spent catalyst from an outlet of the reactor. This may be achieved by the provision of suitable storage for regenerated catalyst or by use of a regenerator which is shared by two or more reactor trains, e.g. the catalyst from a converted unit is regenerated in the regenerator of a second reformer unit in which the regenerator is integrated with the (second) reactor train but
25 not with the first reactor train, i.e. the regenerator for the converted unit is a non-dedicated regenerator. A shared regenerator may be fully integrated with one reactor train but constructed so that it has the capacity to regenerate the catalyst from two or more reactors. The non-integrated reactors may be on-site (same refinery plant) or at remote sites. In this way, the substantial capital cost of the regenerator is
30 proportionately reduced because of the economies of scale associated with regeneration facilities.

[0022] The conversion of a fixed bed (semiregenerative or cyclic) reformer unit to operation with moving-bed reactors may include the replacement or conversion of at

least one fixed-bed reactor and preferably all of the fixed bed reactors in the unit to moving-bed reactors. The catalyst facilities of the converted unit and the continuous moving-bed reactors will be operatively connected with existing plant equipment, as necessary. The moving bed reactors may be disposed in a side-by-side or stacked arrangement, depending on site requirements. The conversion does require addition of catalyst loading, recovery (unloading) and transfer facilities associated with the interface between the continuous reactor(s) and the regeneration facilities which have been selected, that is, off-site, non-integrated on-site or partly integrated (shared regenerator) regeneration.

[0023] The spent catalyst recovered from the reforming unit may be collected and transferred to an offsite regeneration facility. Preferably the catalyst may be recovered in a continuous manner. The spent catalyst that exits the last reactor will be collected in a spent catalyst storage container and then transferred in smaller batches to drums or special containers suitable for transportation to an offsite regeneration facility.

[0024] The catalyst may be collected in storage devices (drums, containers, vessels) and transferred to the regeneration facility. The facilities for collecting and transferring the spent catalyst may differ. For example, they could be as simple as a dump nozzle at the bottom of the last reactor emptying into conventional 200 litre (55 US gallon) drums. Alternatively, they could include specially designed trucks, rail cars, or shipping containers capable of maintaining an inert atmosphere during loading, transportation and unloading.

[0025] The catalyst regeneration facility can be an offsite or an onsite facility preferably centrally located if site conditions permit. In most cases the regeneration facility will preferably be independent and only indirectly associated with a particular reforming unit although the shared regenerator configuration may be possible and even desirable in certain circumstances. Independent regeneration facilities will thus operate autonomously from any particular reforming unit and may regenerate catalyst from one or more reforming units. This will allow for increased operational flexibility for the reforming units as well as the regeneration facility, lower investment cost (on unit basis) and improved reformat product. According to this embodiment a centrally located catalyst regeneration facility receives spent catalyst from a plurality of moving-

bed reformers continuously or intermittently and supplies the reactors of these units continuously or intermittently with regenerated catalyst.

5 **[0026]** Any typical reforming catalyst may be used, including those comprising one or more Group VIII noble metals on a refractory support. The catalyst will contain a hydrogenation-dehydrogenation function (hydrogen transfer) and an acid function. Examples include catalysts comprising platinum, tin, rhenium, iridium, tin or combinations of these metals. A preferred support includes substantially spherical alumina support particles. A preferred catalyst comprises platinum, platinum and tin,
10 or platinum and rhenium on substantially spherical alumina support particles. Spherical particles are preferred for movement through the moving bed reactors and other equipment with minimal attrition.

15 **[0027]** Any type of regeneration facilities may be used. One preferred regeneration facility may include a continuous moving-bed regeneration tower characteristic of commercially available continuous reforming processes or it may include a batch regeneration process unit. One example of a batch regeneration process is the Hot Flue Gas Regeneration Circuit characteristic of Cyclic POWERFORMING™. Another example is a shut down semiregenerative unit used
20 exclusively for catalyst regeneration.

25 **[0028]** A suitable regeneration procedure may include a hydrocarbon purge, coke burn, oxy-chlorination, oxides purge, and reduction procedure. However, depending on the type of catalyst it may also include presulfiding as part of the regeneration procedure. It may be preferable to complete the reduction and presulfiding (if necessary) after the regenerated catalyst has been returned from the offsite regeneration facility immediately before feeding the regenerated catalyst to the top of the lead reactor. The oxy-chlorination procedure may vary significantly. At a minimum it may include the addition of a chloride containing agent such as Cl_2 , HCl , or a
30 pumpable organic chloride after the coke burn to replace the chloride lost during the coke burn. However, it may also include a continuous addition of a chloride agent during the coke burn. It may also include over-chlorination after the coke burn followed by a chloride equilibration step after the platinum metal has been thoroughly

redispersed. The actual regeneration procedure might include any combination of these chlorination techniques.

5 [0029] Figure 1, given for example only, shows a continuous catalytic moving-bed reforming process unit 10. This unit is built from an existing high pressure semiregenerative reformer unit by removing the fixed bed reactor cases and installing moving bed cases which are deployed in a side-by-side arrangement. If site requirements, for example, limited area, dictate, a stacked reactor configuration could well be used with a consequent reduction in catalyst transfer equipment as the lift pots and transfer lines shown in Figure 1 could simply be replaced by gravity trickle from one reactor to the next reactor in the train. In Figure 1, thicker lining indicates new equipment and piping while thinner lining indicates existing equipment and piping.

15 [0030] The conversion includes replacing each semiregenerative reactor (not shown) with a new moving-bed reactor 27, 57, 65, installing a fresh/regenerated catalyst loading platform 18, a fresh catalyst storage drum 20 which can be fed with fresh/regenerated catalyst through line 11 with feed controlled by valve 13. Other newly added items include spent catalyst storage drums 71 and 73, intra-unit catalyst transfer equipment including collectors 24, 54, 64, lift pots 31, 61, 69 and transfer lines 20 53, 58, 59, a spent catalyst loading platform 24, dust filters 26, a N₂ cooler 28, a N₂ circulator 30, make-up nitrogen supply 32 and a H₂ preheater 34. Similar facilities for unloading spent catalyst from the last reactor are shown which include a disengaging hopper 71, lock hopper 73, and loading platform 74. Other additional items re discussed below. The following existing equipment items are retained and reused in 25 the converted unit: charge furnace 36, reheat furnaces 38, 40, feed/effluent heat exchanger 42 and associated lines, effluent cooler 44 and associated lines, product separator 46, recycle compressor 48 and chloride treaters 50.

[0031] In operation the converted unit operates as follows:

30 Fresh catalyst or regenerated catalyst from the offsite regeneration facility is placed on loading platform 18 and added to the regenerated catalyst storage drum 20. The catalyst then enters the lock hopper 17 where it is purged with nitrogen from line 15 to remove residual air. The catalyst is then transferred to the lift engager 19 where it is

lifted with hydrogen gas fed through line 19 and valve 21 to reduction/purge/
disengaging chamber 12 on top of first reactor 27 by way of transfer line 52. Gas is
removed from hopper 12 in elutriation tube 12 and passes through line 43 to dust
filters (new) 26. Reduced catalyst is added to the first reactor 27 via catalyst flow lines
5 37. Catalyst moves by gravity downwards in reactor 27 until it exits through lines 41
and enters catalyst collector 24 which is fed with hydrogen rich gas through line 39.
Catalyst from catalyst collector 24 then enters lift engager 31 where it is lifted with a
H₂ rich stream to disengaging hopper 55. Lift gas is admitted through valve/inlet 33.
The catalyst enters the second disengaging hopper 44 atop second reactor 57 after
10 which it enters reactor 57 where it moves downward to the outlet and passes into
catalyst collector 54, followed by lift engager 61. Catalyst from lift engager 61 is then
lifted with a hydrogen rich gas to disengaging hopper 16 atop third and last reactor 65
from which it then passes to the inlet of the third and last reactor 65. Catalyst flows
downward through reactor 65 to collector 64 and then to lift engager 69. Catalyst from
15 lift engager 69 is lifted with a hydrogen rich gas to disengaging/storage drum 71 in
which gas is separated from the catalyst and passes through elutriation tube 22 to dust
filter 26. The spent catalyst is then transferred to lock hopper 73 where it is purged
with nitrogen and finally loaded into the shipping containers on Spent Catalyst Loading
Platform 24.

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[0032] The reformer charge enters the unit at inlet 85 and passes through line 82
picking up hydrogen rich recycle gas from line 83 to effluent heat exchanger 42 and
then to pre-heat furnace retained from the original unit. From pre-heat furnace it
passes into contact with the catalyst in first reactor 27. After passage through first
25 reactor 27 it passes in turn through re-heat furnace 38 (also a retained item) to second
reactor 57, through reheat furnace 40 (retained) and finally to third reactor 65.
Reformate effluent from the third reactor is taken via line 89 to charge heat exchanger
42 and recycle hydrogen heat exchanger 34 to effluent cooler 44 and then via line 88
to the existing product separator 46 in which liquid and as are separated. Hydrogen
30 rich gas is recompressed in compressor 48 fed through line 77 and passes either as
recycle gas through line 83 back to the unit or out through existing chloride treaters 50
to the refinery. Unstabilized reformate is recovered through line 75.

5 [0033] Nitrogen for purge is introduced through make up inlet 32 and passes to the nitrogen loop via knock out drum 45 and then through line 51 to lift engager 17 with nitrogen also being introduced into lock hopper 23 through line 15. Gas from the reactors passes through the dust filters 26 to nitrogen cooler 28 before returning to the nitrogen loop through knock out drum 45.

10 [0034] Figure 1 does not depict the actual offsite or centrally located on-site regeneration facilities. Several different designs for these regeneration facilities may be used. A preferred design is likely to vary based on the actual project specifics. Options for offsite regeneration systems may include:

- 1) facilities already available from commercial catalyst regeneration companies;
- 2) continuous moving-bed regeneration technology;
- 15 3) commercially available cyclic regeneration facilities including Hot Flue Gas Technology offered by ExxonMobil POWERFORMING Technology; or
- 4) idle existing semiregenerative catalytic reformer of various configurations dedicated to completing catalyst regeneration.

20 [0035] Variations of the present method may include:

- 20 1) sending all spent catalyst removed from the outlet of the last reactor to a third party catalyst vendor who will regenerate the catalyst for a fee;
- 2) building an oversized regeneration facility as part of a conversion project for an existing semiregenerative reformer. The facility may be sized to regenerate catalyst from other units that may also be converted;
- 25 3) build an oversized regeneration facility at some central location and size it to regenerate catalyst from other semiregenerative reformers in the region that will be converted;
- 30 4) use an existing idle semiregenerative reformer or move those idle facilities to some more appropriate location to regenerate the spent catalyst from other operating semiregenerative reformers in the region that will be converted; and

- 5) expand existing regeneration facilities at one or more locations that already use continuous catalytic regeneration technology so that the onsite facilities at that site (or sites) can also regenerate catalyst from other units (in addition to the catalyst that they currently regenerate from their own integrated unit).

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EXAMPLE

[0036] Table 1 presents results of a feasibility study to evaluate the unit of Figure 1.

TABLE 1

	Semiregenerative Process Before Revamp	Revamp with Offsite Regeneration (Figure 1)
Feed Rate, m ³ /day (kbd)	4,770 (30)	5,406 (34)
Severity, RON	95	100
Reactor Pressure, kPag (psig)	3344 (485)	2482 (360)
C ₅ + Yield, LV%	72.5	72.1
H ₂ Production, n.l.l. ⁻¹ (SCF/B)	77 (435)	130 (733)

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[0037] Reactor pressure is reduced about 25 percent, from 3344 to 2482 kPag (485 to 360 psig) despite an increase in feed rate from 4,770 to 5,406 m³/day (30 to 34 kbd). This reduction in reactor pressure allows the refiner to maintain a relatively constant C₅+ reformat yield despite a severity increase from 95 to 100 RON. Hydrogen production also increases by almost 70% from 77 to 130 n.l.l.⁻¹ (435 to 733 scf/B).

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[0038] Catalyst regeneration facilities may be used to regenerate spent catalyst from more than one reformer, thus achieving economies of scale and (2) to achieve somewhat more modest pressure reductions and yield improvements, but at a significantly lower project investment than existing conversions with dedicated continuous catalyst regeneration facilities.

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